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MAIN AND TRACE ELEMENTS IN GROUNDWATER FROM THE QUATERNARY SEDIMENTS IN THE SOUTHERN GREAT PLAIN, HUNGARY

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ABSTRACT

Chemical composition of groundwater samples from the southern part of the Great Hungarian Plain was determined. Cluster analysis based on major elements, and based on minor and trace elements resulted in similar separation of the study area. The units correspond to three hydrogeological regions: the River Körös basin, the River Maros alluvial fan and the River Danube deposits. Processes controlling both major and trace element concentrations are dissolution of carbonate minerals, ion exchange, oxidation-reduction, albite weathering and formation of secondary minerals. In the Körös basin water movements is restricted. In the River Maros alluvial fan the direction of water flow is from south-southeast to north-northwest, and in the River Danube deposits it is from west to east.

INTRODUCTION

In the Quaternary sediments of the Great Hungarian Plain there are two chemically distinct types of groundwater: Ca-Mg-HCO_3 type and Na-HCO_3 type. In the Ca-Mg-HCO_3 type waters the concentration of total dissolved solids is low while in the Na-HCO_3 type waters it is much higher. The processes controlling major and trace element concentrations in groundwater are dissolution and precipitation of carbonate minerals, feldspar weathering (PACES 1973, CHOU and WOLLAST 1984, BERNER 1981, MURPHY and HELGESON 1987), redox reactions and ion exchange (CHAPELLE and KNOBEL 1983, APPELO et al. 1989).

Carbonate minerals are much more soluble in waters than silicates. Dynamic interfaces between aqueous solutions and carbonate minerals lead to reversible dissolution-precipitation reactions. Thermodynamic control of equilibrium can be applied to carbonates if they react rapidly on the time scale of a hydrological system. According to HOCHELLA (1990), during dissolution the near surface of calcite remains ordered. Sr, Ba and Mn are often built in carbonate minerals. Magnesium is partially replaces by Mn in dolomite, while Sr and Ba can substitute for Ca in the structure of calcite. As precipitation of dolomite from most natural waters does not control Mg concentration in fresh water (HEM 1985), equilibrium can be reached only from undersaturation. According to STUMM and MORGAN (1981) calcite has a tendency to accommodate Mg^{2+} in its structure to form magnesian calcite. So precipitation of Ca and Mg as magnesian calcite may be a more likely process than dolomite precipitation.

The surface of feldspar is covered by leached layer and secondary minerals (DAVIS and KENT 1990). The feldspar dissolution is an irreversible process. CO_2 plays an important role both in carbonate and silicate dissolution reactions. The solubility of albite depends on the partial pressure of CO_2. If albite dissolves under the influence of CO_2 the resulting solution is

characterized by HCO_3^-, Na and H_4SiO_4 (STUMM AND MORGAN 1981). Na concentration derived from the hydrolysis of albite increases with the relative surface area of albite (HELGESON 1971). The first process to occur when albite interacts with water is a rapid exchange of H^+ for Na^+ (HELLMANN et al. 1989, HELGESON et al. 1984, ALTHAUS and TIRTADINATA 1989). This initial reaction of feldspar is accompanied by increasing pH (BUSENBERG and CLEMENCY 1976), and it proceeds even at neutral and slightly basic pH conditions (CASEY and BUNKER 1990). However feldspar weathering is an irreversible process (HELGESON 1971) the composition of the resulting solution is controlled by the equilibrium among highly disordered reaction products and the aqueous phase. In silicate minerals Mn replaces Fe and Mg, Sr substitutes for Ca and Ba, and K is often replaced by Ba. A possible diadochy can occur between Li and Al, Fe(II) and especially Mg (WEDEPOHL et al. 1964, FAURE et al. 1967). In the groundwater the concentration of these metal ions are influenced by ion exchange processes on the cation-specific surface sites of calcite. Metal ion sorption depends on aqueous Ca concentration (DAVIS et al. 1987, COMANS and MIDDELBURG 1987, WERSIN et al. 1989, ZACHARA et al. 1991). The concentration of Li is primary controlled by incorporation into clay minerals (HEIER and ADAMS 1964, BILLINGS et al. 1964). The coprecipitation of Li with calcium carbonate can play an important role in the distribution of Li in groundwater (OKUMURA and KITANI 1985). Wheathering of silicate minerals can be considered as a main source of Si and Al. The solubility of silicate minerals is pH dependent. Aluminium is insoluble at neutral pH, it precipitates as gibbsit, or enters the clay minerals forming in the aqueous system (APPELO 1993).

Manganese and iron oxyhydroxides of sediments have an importance in the distribution and mobility of trace elements. Trace elements associated with Mn and Fe oxyhydroxides are released during reductive dissolution of the oxides, while the oxidation of metal oxyhydroxides can remove trace elements from solution by adsorption or coprecipitation (BALLISTRIERI and MURRAY 1994). In the trace metal adsorption significant role is played also by calcite, clay minerals and organic matter (TESSIER et al. 1980, LION et al. 1982, ZACHARA et al. 1991).Humic substances influence the complexation of trace elements with metal oxides, especially at low pH values (DAVIS and LECKIE 1978, LAXEN 1985).

The aim of this work is to separate the aquifer systems in the Pleistocene sediments of the southern part of the Great Hungarian Plain on the basis of the major and trace chemical components in groundwater, and to establish the processes controlling the chemical features of groundwater in the different aquifers.

LOCATION AND GEOLOGY

The study area is located in the southern part of the Great Hungarian Plain (*Fig.1.*) which is the biggest sedimentary basin in Europe that is filled with Neogene and Quaternary sediments of great thickness. The geological evolution of the Pannonian Basin started in the Miocene with the uplift of the Carpathian mountains and the subsidence of the enclosed area (RÓNAI 1985). Tectonic activity continued at different rates throughout the area; therefore, the thicknesses of the sediments are variable. The deepest part of the study area is the Makó-Hódmezővásárhely depression where the thickness of the sediments is more than 5000 m, of which 2000-3000 m are marine sediments, and 1000-2000 m are lake sediments which were deposited after the outlet of the basin to the Mediterranean sea had closed. The hydrogeological features are controlled by structures active in the Tertiary and Quaternary periods. During the Pliocene 2000-3000 m thick marine sediments:

conglomerate, sandstone, marl and clay, then 1000-2000 m thick lake sediments: sand, silt and clay were deposited. Going upwards the sedimentary sequence grades into variegated clay which represents the uppermost part of the Pliocene sedimentary series.

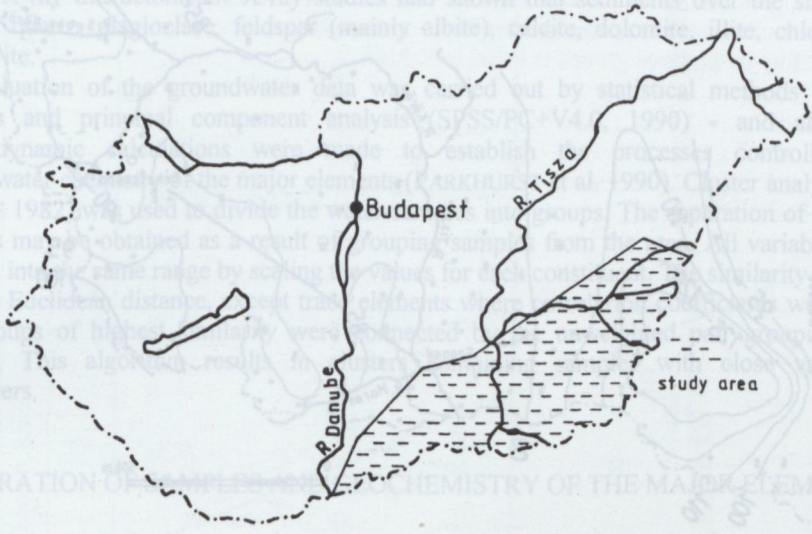

Fig. 1. Location of the study area

Towards the end of Pliocene, the basin was uplifted. Fluvial sedimentation started in the inner part of the basin about 2.4 million years ago, at the beginning of the Quaternary. Local scale tectonic events together with climatic differences determined the cyclic fluvial sedimentation during the Pleistocene. In the Early Pleistocene, 300-450 m of fluvial sediments were deposited in the deepest local sub-basins. The areas between local depressions sank as much as several tens of meters. These sediments generally consist of gravel, sand, silt and clay layers, 20-50 m in thickness. The number and the thickness of sand layers are greater than in the Middle and Upper Pleistocene. Cyclicity in grain size composition of the layers can be correlated with vertical Quaternary tectonic movements. The vertical movements produced a deep local depression in the northeastern part of the study area. This depression was filled up with fine grained material by the Rivers Körös and Berettyó: fine sand, silt and clay. These Quaternary strata are 500-550 m thick and form the lowest yielding artesian aquifer within the Southern Great Plain. In the western part of the area the River Danube deposited material during the Quaternary period. The Pleistocene formation consists of 50-70% highly permeable sand with silt and clay (ERDÉLYI 1976).).

The potentiometric contours of the Pleistocene aquifers to the depth of between 200-400 m determined by ERDÉLYI (1979) on the basis of water level elevation in drinking water wells before withdrawal, indicate that in the Pleistocene layers groundwater generally flows from west to east in the River Danube deposit, in the south-southwestern part of the study area, however no lateral water flow is supposed in the Körös basin (*Fig.2.*). The multi-layer aquifer system of the Great Hungarian Plain consists of two flow-regions. One of them is an intermediate flow-region in the upper part of the basin composed predominantly of loose clastic Quaternary sequences. The other one is in the deeper, thermal aquifer system.

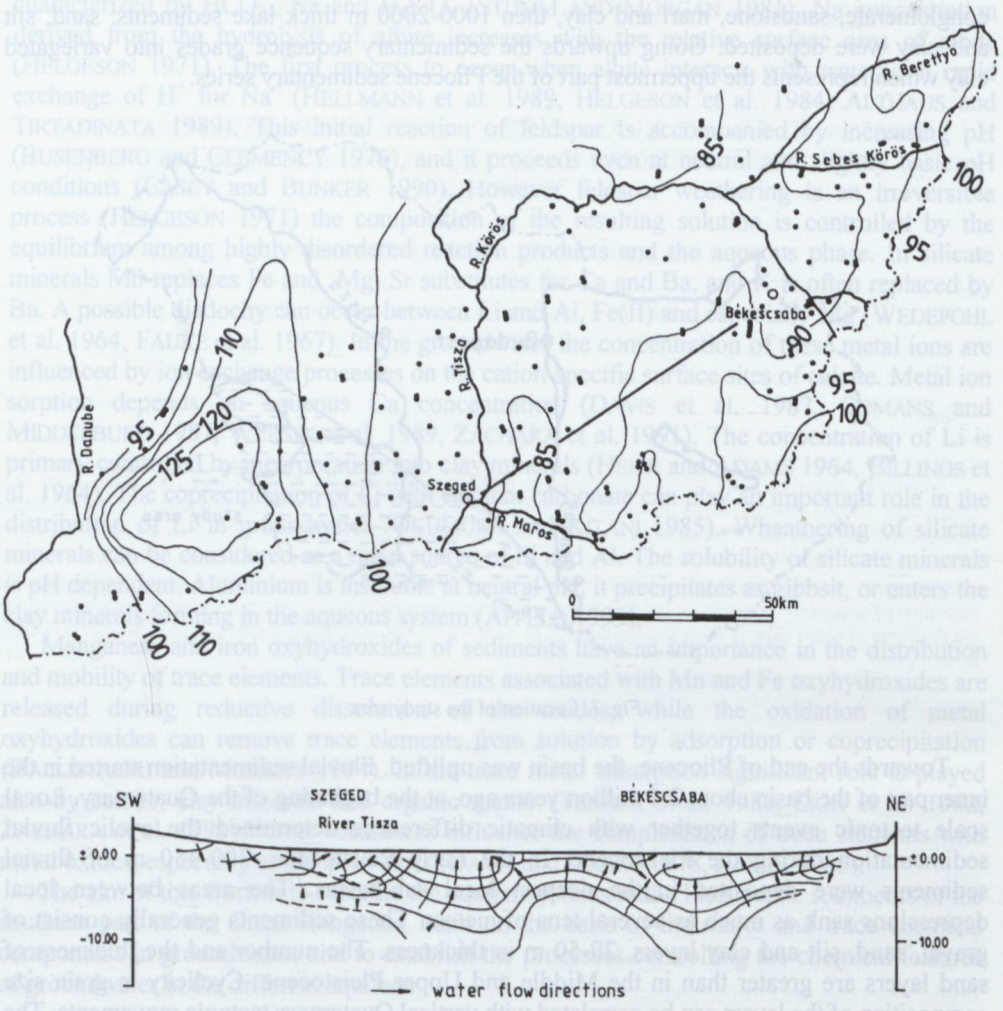

Fig. 2. The piezometric contours and water flow directions by ERDÉLYI (1976) and the location of the studied wells.

METHODS

In situ measurements and laboratory major, minor and trace element analyses were used to establish the geochemical evolution of groundwater in the studied aquifers. Groundwater samples were obtained from municipal water supplies. Field determinations of pH and temperature were made. Groundwater samples from water wells of different depths (40-600 m) were collected, cooled and analyzed within 24 hours. Conductivity, pH, hardness, alkalinity, Ca, Mg, Na, K, Fe, Mn, ammonium, chloride, and chemical oxygen demand (COD) were determined in 142 samples, and in most of them (109 samples) As, Zn, Ba, Sr, Li, Si, Al were also analysed. The analysis were performed at the Hungarian Geological Survey, Budapest, at the Horticulture University, Budapest and at the Institute of

Public Health, Szeged. Procedures for making determinations are summarized as follows: hardness, alkalinity, COD and chloride by titration; ammonium by spectrophotometry; Na, K, Ca, Mg, Fe, Mn, Zn, Ba, Sr, Li, Si, Al, and phosphate by ICP-AAS, and As by AAS-hydrid method. 22 core samples of 61-468 m depth were subjected to XRD analysis using a DRON-UM 1 X-ray diffractometer. X-ray studies had shown that sediments over the study area contain quartz, plagioclase, feldspar (mainly albite), calcite, dolomite, illite, chlorite and muscovite.

Evaluation of the groundwater data was carried out by statistical methods - cluster analysis and principal component analysis (SPSS/PC+V4.0, 1990) - and afterwards thermodynamic calculations were made to establish the processes controlling the groundwater chemistry of the major elements (PARKHURST et al. 1990). Cluster analysis (LE MAITRE 1982) was used to divide the water samples into groups. The separation of different aquifers may be obtained as a result of grouping samples from the area. All variables were brought into the same range by scaling the values for each constituent. The similarity measure was the Euclidean distance, except trace elements where correlarion coefficients were used. The groups of highest similarity were connected by the unweighted pair group average method. This algorithm results in clusters containing samples with close values of parameters.

SEPARATION OF SAMPLES AND GEOCHEMISTRY OF THE MAJOR ELEMENTS

The present study discusses the main and trace element distribution in water samples collected from the Pleistocene layers, in the southeastern part of the Great Hungarian Plain. Location of wells, the piezometric contours and the direction of groundwater flow path are given in *Fig.2.* The major cations are Ca, Mg and Na, the major anions are dominated by HCO_3. On the basis of the frequency distributions of the components it was established that groundwater quality is not uniform throughout the study area. Samples represent more than one population. This possibly means that different processes play a role in determining the chemical composition of groundwater from different depths or locations.

Separation of samples based on the distribution of the main mono- and divalent cations was performed. Flow systems were characterized by cation exchange on clay minerals. Ion exchange has fundamental importance in water-rock interactions. Along the flow path the distribution of the dissolved components may follow a chromatographic pattern because of the differences in retardation for the various cations. Along the flow path the concentration of Na increases while the concentration of divalent cations - Ca and Mg - decreases. There is a linear trend with a slope of -2 between the molar concentrations of mono- and divalent cations (VARSÁNYI and Ó. KOVÁCS, 1997). The molar concentration of Na against Ca + Mg is shown in *Fig.3.* Data appear to be scattered around two lines. It suggests that at least two ion exchange systems with different Na concentrations exist over the study area. To draw lines between water samples belonging to the different flow systems in which ion exchange takes place cluster analysis was performed with three variables. Two of them are X and Y coordinates of the location of water wells. The third variable is the distance between each point in *Fig.3.* and a line with a slope of -2. These distances are similar for the samples belonging to the same water flow system but they differ from those of the other water flow system with different ion concentration. However under natural conditions the effect of ion exchange prevails only statistically because factors other than ion exchange modify the concentration of mono- and divalent cations. These distances appear suitable variables to

separate water flow or aquifer systems (VARSÁNYI and Ó. KOVÁCS, 1994). Cluster analysis resulted in three main groups which are shown in *Fig.4./a.* By their location, the groups correspond to the geological regions established by RÓNAI (1985) i.e. Group A to the River Körös basin (black diamond), Group B to the alluvial fan of the River Maros (black square) and Group C to the River Danube deposits (open symbols) located in the region between the Rivers Danube and Tisza, and the southern section of the River Tisza valley. The average water quality in the three groups is listed in Table 1.

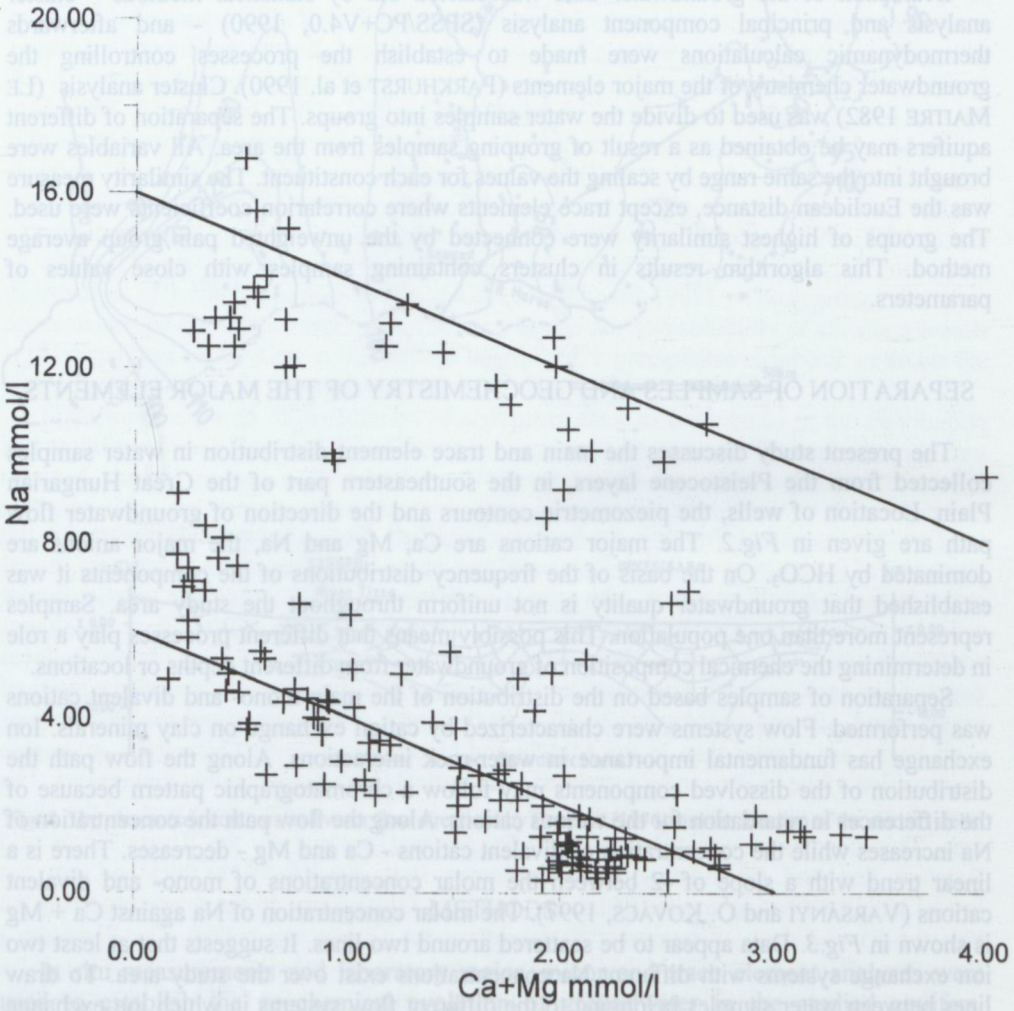

Fig. 3. Relationship between the molar concentrations of Na and the sum of Ca and Mg.

In order to understand what reactions control the major element composition of groundwater in the three geological regions, PHREEQE (PARKHURST et al. 1990) was used to perform the simulation (VARSÁNYI AND Ó. KOVÁCS, 1994). On the basis of these simulations it has been established that originally in each group the system is open for CO_2. In these systems calcite, dolomite and albite dissolve. In the River Körös basin the CO_2

TABLE 1

Mean values and standard deviations in the groups separated on the basis of major element.

Water type		Group A, River Körös			Group B, River Maros			Group C, River Danube		
Component	Unit	Mean	s.d.	No. of sample	Mean	s.d.	No of sample	Mean	s.d.	No. of sample
Electric conduct.	uS/cm	1264	202	34	550	158	31	484	93	77
pH		7,88	0,21	34	8,07	0,33	31	7,71	0,27	77
Alkalinity	mequ/l	14,4	1,9	34	6	1,8	31	6,1	1,2	77
Ca	mmol/l	0,8	0,6	34	0,9	0,5	31	1,1	0,5	77
Mg	mmol/l	0,5	0,3	34	0,4	0,2	31	0,7	0,3	77
Na	mmol/l	11,7	2,4	34	3,6	1,5	31	2,6	2,4	77
K	mmol/l	0,05	0,03	34	0,03	0,04	31	0,03	0,01	77
Ammonium	mmol/l	0,16	0,06	34	0,17	0,12	31	0,07	0,04	77
Cl	mmol/l	0,63	0,23	34	0,61	0,13	31	0,13	0,06	77
COD	mg/l	9,9	6,9	34	5,2	3,6	31	2,1	1,5	77
SI calcite		0,64	0,26	34	0,53	0,18	31	0,26	0,2	77
SIdolomite		1,12	0,48	34	0,64	0,38	31	0,34	0,43	77

TABLE 2

Mean values and standard deviations in the groups separated on the basis of minor and trace elements .

Water type		Group 1.			Group 2.			Group 3.		
Component	Unit	Mean	s.d.	No. of sample	Mean	s.d.	No of sample	Mean	s.d.	No. of sample
As	mmol/l	0,00009	0,00011	18	0,00025	0,00014	19	0,00032	0,00023	27
Fe	mmol/l	0,00492	0,00212	18	0,00316	0,00187	19	0,00265	0,00222	27
Zn	mmol/l	0,00016	0,00013	18	0,00021	0,00022	19	0,00009	0,00009	27
Mn	mmol/l	0,00079	0,00017	18	0,00085	0,00070	19	0,00063	0,00075	27
Ba	mmol/l	0,00107	0,00026	18	0,00110	0,00023	19	0,00053	0,00027	27
Li	mmol/l	0,00050	0,00025	18	0,00078	0,00037	19	0,00100	0,00055	27
Sr	mmol/l	0,00336	0,00053	18	0,00514	0,00054	19	0,00178	0,00114	27
Si	mmol/l	0,46006	0,03778	18	0,38163	0,02996	19	0,31964	0,03347	27
Al	mmol/l	0,00000	0,00000	18	0,00000	0,00000	19	0,00000	0,00000	27
Depth	m	318	08.5	18	324	115	19	335,62	129,81	27

Water type		Group 4.			Group 5.			Group 6.		
Component	Unit	Mean	s.d.	No. of sample	Mean	s.d.	No of sample	Mean	s.d.	No. of sample
As	mmol/l	0,00143	0,00066	13	0,00113	0,00034	22	0,00081	0,00040	10
Fe	mmol/l	0,01780	0,00745	13	0,00280	0,00186	22	0,00804	0,00550	10
Zn	mmol/l	0,00026	0,00026	13	0,00013	0,00011	22	0,00154	0,00203	10
Mn	mmol/l	0,00231	0,00101	13	0,00083	0,00066	22	0,00110	0,00079	10
Ba	mmol/l	0,00107	0,00024	13	0,00076	0,00031	22	0,00097	0,00046	10
Li	mmol/l	0,00112	0,00097	13	0,00185	0,00158	22	0,00267	0,00196	10
Sr	mmol/l	0,00431	0,00166	13	0,00203	0,00097	22	0,00223	0,00145	10
Si	mmol/l	0,38131	0,04614	13	0,36800	0,05413	22	0,38180	0,08821	10
Al	mmol/l	0,00000	0,00000	13	0,00000	0,00000	22	0,00258	0,00200	10
Depth	m	153,15	86,93	13	363,91	204,72	22	453,65	410,29	10

pressure remained fairly high (log pCO_2=-1,8) and due to this high CO_2 pressure a large quantity of albite dissolved. In the other two groups the CO_2 pressures were lower (log pCO_2=-2.0 and -2.3 respectively) and lower Na contents were produced. Due to the albite dissolution in the open system, water becomes oversaturated for both calcite and dolomite. The degrees of oversaturation are different in the three groups and they correspond to the Na contents of water. The equilibrium between water, calcite and dolomite seems to be reached only from undersaturation and not from oversaturation. In the River Körös basin and in the alluvial fan of the River Maros the CO_2 pressure decreases from the shallower to the deeper layers, the system becomes closed and albite dissolution proceeds. pH increases and there is not enough H^+ available for further albite dissolution.

Over the region between the Rivers Danube and Tisza and in the southern section of the River Tisza valley (in the River Danube deposits) the system was initially open. Less albite dissolved in relation to the River Körös basin. The reason for the smaller Na concentration in this group may be the lower partial pressure of CO_2, the shorter exposure of feldspar to the water in the open system and the lower ratio of the reactant mineral surface area to the volume of the aqueous phase. It was supposed that along a west-east flow path ion exchange is the main process, albite dissolution under the closed system conditions does not play an important role in controlling water quality. Within the study aquifer Na is exchanged to Ca and Mg on the clay minerals and equilibrium with calcite and dolomite is reached.

The relationship between alkalinity, calcium, magnesium and sodium concentrations suggests three sub-types of water in the River Danube deposits. Along the W-E flow path significant changes in the concentrations of the main cations occur which may be summarized as follows:

1. The samples with the highest water hardness (calcium plus magnesium concentrations are up to 2.75 mmol/l) are situated in the western part of the study area (open circles in *Fig.4./a*). The variation in alkalinity is related mainly to calcite and dolomite dissolution. This is the recharge area (ERDÉLYI, 1979) and the beginning of the groundwater flow system. Dissolved sodium content is supposed to originate from irreversible feldspar weathering. Dissolution of carbonate minerals is an equilibrium process which is controlled by CO_2 partial pressure while sodium concentration depends on the reaction rate and time.

2. From the chemical point of view this is a transitional zone between the beginning and the end of the flow path (open diamonds in *Fig.4./a*). The sum of calcium and magnesium concentrations changes between 0.5 and 2.5 mmol/l, and the sodium concentration between 5.5 and 0.3 mmol/l. The mirror image of mono and bivalent cations (*Fig.3.*) and the almost constant alkalinity show that ion exchange controls water chemistry along this part of the flow path.

3. The water samples having the lowest calcium and magnesium and the highest sodium concentrations are situated in the eastern part of the River Danube deposits, around Hódmezővásárhely (open squares in *Fig.4./a*). Ca and Mg concentrations are constant, Na concentration is increasing with alkalinity. In this group of samples the mean alkalinity is higher (7.7 meq/l) than it is in the samples from the recharge area (5.9 meq/l). The increase in alkalinity demands an additional carbon source. In spite of the availability of organic material in the sediments (TOC varies from 0.02% to 0.5%, mean value is 0.1%), the in situ CO_2 production through oxidation is limited by the availability of oxidizing agents. However, an anaerobic, microbially mediated disproportioning of organic matter may result in CO_2 (BRONS et al., 1991). Both the transformation of organic matter and the mixing of recharge water with older formation water may be the processes

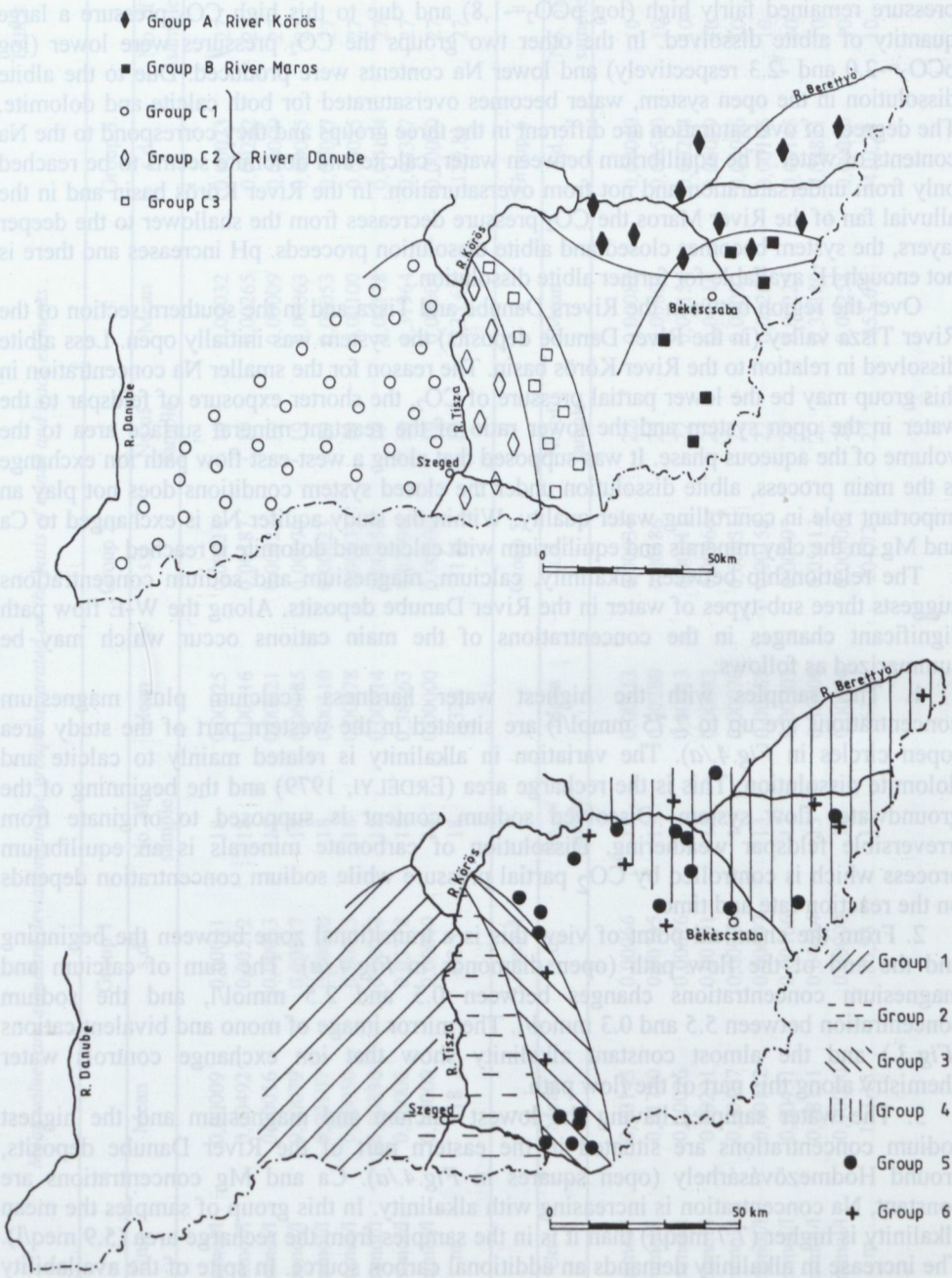

Fig. 4. Location of the groundwaters characterized by different water quality
a) separaion on the basis of major elements b) separaion on the basis of minor and trace elements

which resulted in the increase in alkalinity. This sodium-bicarbonate type water is located in the discharge area of the water flow system (ERDÉLYI, 1979).

Changes of sodium concentration from west to east and from south to north are given in *Fig.5.* and *Fig.6.* In the River Körös basin neither piezometric contours nor water chemistry show infiltration. On the basis of the piezometric contours it is a discharge area. In the River Maros alluvial fan sodium concentration is increasing from south to north, and this increase corresponds to the water flow direction. In the River Danube deposits the increase in Na concentration indicate a west-east flow direction.

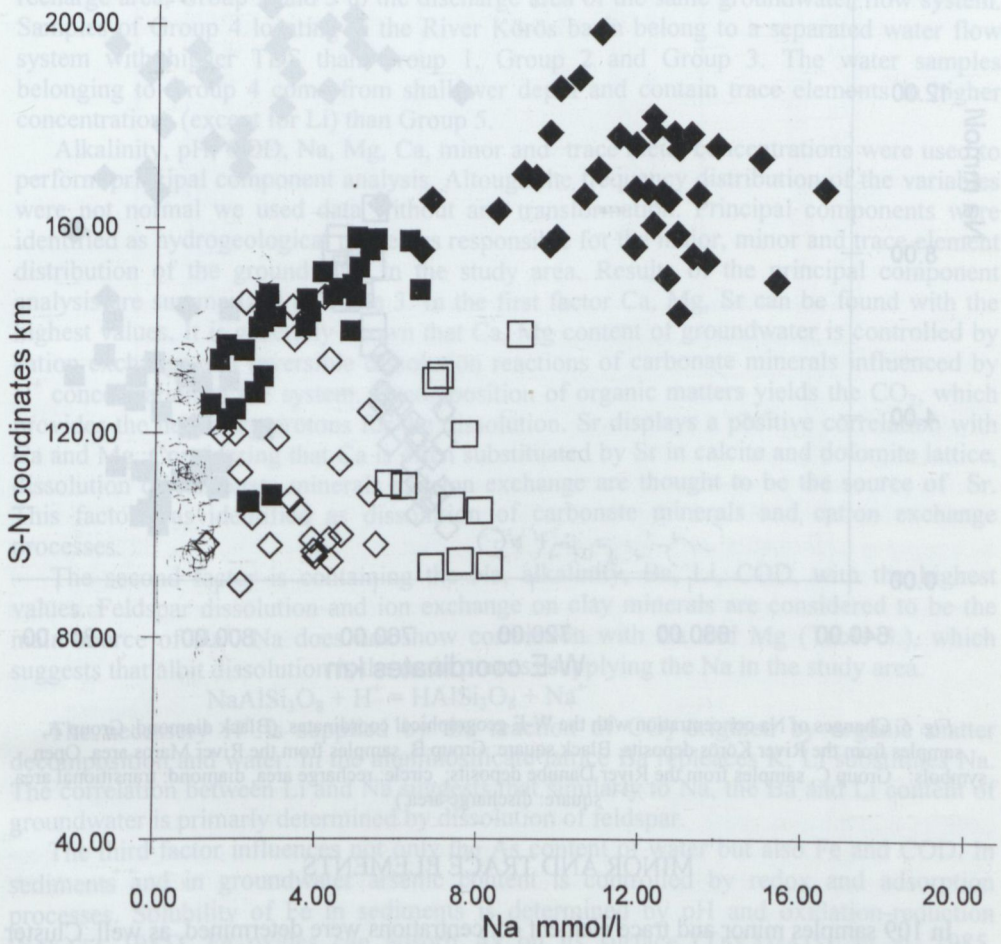

Fig. 5. Changes of Na concentration with the S-N geographical coordinates. (Black diamond: Group A, samples from the River Körös deposits. Black square: Group B, samples from the River Maros area. Open symbols: Group C, samples from the River Danube deposits; circle: recharge area, diamond: transitional area, square: discharge area.)

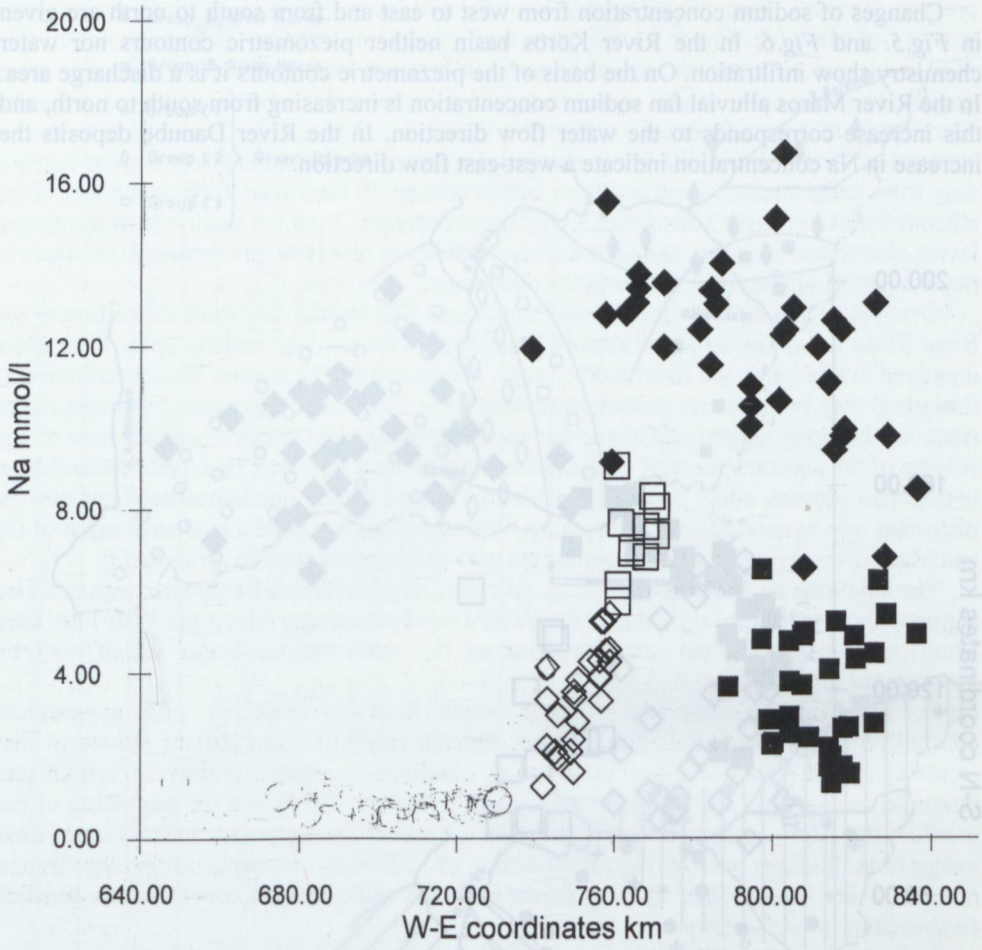

Fig. 6. Changes of Na concentration with the W-E geographical coordinates. (Black diamond: Group A, samples from the River Körös deposits. Black square: Group B, samples from the River Maros area. Open symbols: Group C, samples from the River Danube deposits; circle: recharge area, diamond: transitional area, square: discharge area.)

MINOR AND TRACE ELEMENTS

In 109 samples minor and trace element concentrations were determined, as well. Cluster analysis based on the concentrations of nine minor and trace elements resulted in six main groups which are shown in *Fig.4./b*. Mean values and standard deviations of the minor and trace elements in these groups are summarized in Table 2. Four of the six groups correspond to the geological regions: Group 1, Group 2 and Group 3 to the River Danube deposits, Group 4 to the River Körös Basin. Trace element analysis are not available from the River Maros alluvial fan. Location of Group 1, Group 2 and Group 3 in the River Danube deposits correspond to the location of the Ca-Mg bicarbonate, transitional and Na bicarbonate water type, i.e. the recharge and discharge areas. Group 5 and Group 6 are located in the River Körös basin and in the discharge area of the River Danube water flow

system. Group 5 consists of samples with the highest arsenic content, and in the River Körös sediments it corresponds to the deepest samples from about 350 m depth. Group 6 consists of samples with the highest Al concentrations. Based on the similar distribution of groups separated by main and trace elements it is supposed that processes controlling the main and trace element contents are similar.

In the River Danube deposits, where the changes in the concentration of the major elements indicate a west-east water flow direction, from west to east the COD, Si and Fe desrease together with Ca and Mg, while Na, As and Li increase. Group 1 belongs to the recharge area, Group 2 and 3 to the discharge area of the same groundwater flow system. Samples of Group 4 locating in the River Körös basin belong to a separated water flow system with higher TDS than Group 1, Group 2 and Group 3. The water samples belonging to Group 4 come from shallower depth and contain trace elements in higher concentrations (except for Li) than Group 5.

Alkalinity, pH, COD, Na, Mg, Ca, minor and trace metal concentrations were used to perform principal component analysis. Altough the frequency distribution of the variables were not normal we used data without any transformation. Principal components were identified as hydrogeological processes responsible for the major, minor and trace element distribution of the groundwater in the study area. Results of the principal component analysis are summarized in Table 3. In the first factor Ca, Mg, Sr can be found with the highest values. It is generally known that Ca, Mg content of groundwater is controlled by cation exchange and reversible dissolution reactions of carbonate minerals influenced by H^+ concentration of the system. Decomposition of organic matters yields the CO_2, which provides the necessery protons for the dissolution. Sr displays a positive correlation with Ca and Mg. Considering that Ca is often substituated by Sr in calcite and dolomite lattice, dissolution of carbonate minerals and ion exchange are thought to be the source of Sr. This factor was identified as dissolution of carbonate minerals and cation exchange processes.

The second factor is containing the Na, alkalinity, Ba, Li, COD, with the highest values. Feldspar dissolution and ion exchange on clay minerals are considered to be the main source of Na^+. Na does not show correlation with Ca and Mg (Table 3.), which suggests that albit dissolution is the main process supplying the Na in the study area.

$$NaAlSi_3O_8 + H^+ = HAlSi_3O_8 + Na^+$$

The necessery H^+ is supplied by the reaction of CO_2 origined by organic matter decomposition and water. In the aluminosilicate lattice Ba repleaces K, Li substitutes Na. The correlation between Li and Na suggests that similarly to Na, the Ba and Li content of groundwater is primarly determined by dissolution of feldspar.

The third factor influences not only the As content of water but also Fe and COD. In sediments and in groundwater arsenic content is controlled by redox and adsorption processes. Solubility of Fe in sediments is determined by pH and oxidation-reduction (SAKATA 1985). Fe oxides can adsorb As on its surface (TAKAMATSU et al. 1985, NEWMAN et al. 1985). Oxidative degradation of organic matter is carried out with O_2, NO_3^-, MnO_2, Fe_2O_3 és SO_4^{2-} in consecutive steps (FROEHLICH et al. 1979). Quantity of the burried organic matters can be brought in connection with the velocity of sedimentation (WILSON 1985). At higher velocity of sedimentation the oxigen is comsumed by organic matters and NO_3^-, MnO_2, Fe_2O_3 és SO_4^{2-} become oxidising substances. Fe is reduced and ferrous iron goes into solution which results mobilisation of arsenic. According to this above, this factor was connected with oxidation and reduction.

TABLE 3

Results of the principal component analysis (λ is Eigenvalue).

factors	I.	II.	III.	IV.
Alkalinity	-0.333	0.731	0.308	-0.166
pH	-0.726	0.121	0.095	0.023
COD	-0.043	0.671	0.491	-0.003
Na	-0.418	0.760	-0.096	-0.196
Ca	0.952	0.023	0.037	0.039
Mg	0.940	0.054	-0.104	0.013
As	0.051	0.242	0.719	-0.059
Fe	0.508	0.305	0.533	-0.073
Zn	0.087	0.173	0.337	0.657
Mn	0.481	0.029	0.422	-0.103
Ba	0.409	0.702	-0.395	0.053
Li	-0.218	0.695	-0.414	0.035
Sr	0.854	0.234	-0.135	-0.025
Si	0.172	0.506	-0.597	0.213
Al	-0.245	0.043	0.140	0.679
λ	4.142	3.055	2.180	1.031
λ%	38.2	28.2	20.1	9.5

Al and Zn show the highest value in the fourth factor. Al may go into solution by weathering of silicates. Solubility of Al species depends on pH. Aluminium is insoluble at neutral pH, that it precipitates from the solution as gibbsite or other minerals. This factor, which influences the Al and Zn content of ground water in the similar way, was considered as a process of formation secondary minerals. Zn concentration of waters is influenced by adsorption on the surface of Al oxides. The pH of the system effects both the solubility of aluminium oxides and the adsorption on its surface. Factors influencing the pH also modify the concentration of Al and Zn in groundwater (COSTON et al., 1995).

CONCLUSIONS

1. The whole study area can be divided into three main parts on the basis of major components dissolved in water. The separation based on the distribution of minor and trace elements resulted in very similar location of groups. This separation corresponds to geological units established earlier: the River Körös Basin, the River Maros alluvial fan, and the River Danube deposits. Water quality is different in the three areas.

2. In the River Körös basin where the potentiometric surface does not indicate infiltration or lateral water flow, the chromatographic pattern of ion exchange cannot be pointed out. Groundwater chemistry suggests restricted water movements.

3. In the River Maros alluvial fan the changes in the concentration of Ca, Mg and Na correspond to a chromatographic pattern, indicating a SSE-NNW water flow direction.

4. In the River Danube deposits, water chemistry supports that the groundwater flow direction, in accordance with the potentiometric surface, is from west to east. Both recharge and discharge areas were identified. Recharge area is characterized by Ca-Mg bicarbonate water type, discharge area by Na bicarbonate water type. Between these two

types of groundwater there is a transitional water type, where the changes in the concentrations of chemical components are the highest.

6. Four geochemical processes were identified by principal component analysis which influence minor and trace element content in groundwater of the study area. The four processes are as follows: calcite and dolomite dissolution together with cation exchange, weathering of aluminosilicate minerals, reduction-oxidation processes, and formation of secondary minerals. Sr is primary controlled by calcite and dolomite dissolution and ion exchange on clay minerals. Ba and Li content is determined by aluminosilicate weathering. Distribution of As and Fe is influenced by oxidation and reduction, while the concentrations of Al and Zn are the result of the formation of secondary minerals.

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REFERENCES

ALTHAUS E. and TIRTADINATA E. (1989) Dissolution of feldspar: The first step. In Water-Rock Interaction (ed. MILES D. L.), pp. 15-17. Balkema, Rotterdam.

APPELO C. A. J., PONTEN J. and BEEKMAN H. E. (1989) Natural ion-chromatography during fresh-/sea water displacements in aquifers: A hydrogeochemical model of the past. In Water-Rock Interaction (ed. MILES D. L.), pp. 23-28. Balkema, Rotterdam.

APPELO C. A. and POSTMAN D. (1993) Geochemistry, Groundwater and Pollution. A. A. Balkema.

BALISTRIERI L. S., MURRAY J. W., PAUL B. (1994) The geochemical cycling of trace elements in a biogenic meromictic lake. Gechim. Cosmoshim. Acta, Vol. 58, pp. 3993 - 4008.

BERNER R. A. (1981) Kinetics of weathering and diagenesis. Reviews in Mineralogy Vol. 8, Kinetics of geochemical processes (eds LASAGA A. C. and KIRKPATRICK R. I.), Chap. 3, pp. 111-135.

BILLINGS G. K., HITCHON B., SHOW D. R. (1964) Geochemistry and origin of formation waters in the western Canada sedimentary basin: Alkali metals. Part 2. In: The geochemistry of subsurface brines . Chem. Geol.Vol. 4, pp. 211-223.

BRONS H. J., GRIFFIOEN J., APPELO A. J. AND ZEHNDER A. J. B. (1991) (Bio)chemical reactions in aquifer material from a thermal energy storage site. Wat. Res. Vol. 25, pp. 729-736.

BUSENBERG E. and CLEMENCY CH. V. (1976) The dissolution kinetics of feldspars at 25 C° and 1 atm CO_2 partial pressure. Geochim. Cosmochim. Acta, Vol. 40, pp. 41-49.

CHASEY W.H. and BUNKER B. (1990) Leaching of mineral and glass surfaces during dissolution. Reviewes in Mineralogy. Vol.23. Eds. M.F. Hochella, A.F. White. Chapter 19. pp. 397-427.

CHAPELLE F. H. and KNOBEL L. L. (1983) Aqueous Geochemistry and the Exchangeable Cation Composition of Glauconit in the Aquia Aquifer, Mariland. Groundwater, Vol. 21, pp. 343-352.

CHOU L. and WOLLAST R. (1984) Study of the weathering of albite at room temperature and pressure with a fluidized bed reactor. Geochim. Cosmochim. Acta, Vol. 48, pp. 2205-2217.

COMANS R. N. J. and MIDDELBURG J. J. (1987) Sorption of trace metals on calcite: Applicability of the surface precipitation model. Geochim. Cosmochim. Acta, Vol. 51, pp. 2587 - 2591.

DAVIS J. A. and LECKIE J. O. (1978) Surface ionization and complexation at the oxide water interface. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. J. Colloid interface Sci.Vol. 67, pp. 90 - 107.

DAVIS J. A., FULLER C. C. and COOK A. D. (1987) A model for trace metal sorption processes at the calcite surface: Adsorption of Cd^{2+} and subsequent solid solution formation. Geochim. Cosmochim. Acta, Vol. 51, pp. 1477 - 1490.

DAVIS J. A. and KENT D. B. (1990) Surface complexation modeling in aqueous geochemistry. Reviews in Mineralogy Vol. 23, Mineral-water interface geochemistry (eds HOCHELLA M. F. JR. and WHITE A. F.), Chap. 5, pp. 177-260.

ERDÉLYI M. (1976) Outlines of the hydrodinamics and hydrochemistry of the Pannonian Basin. Geologica Hungarica. Tom 20. pp. 287 - 309.
ERDÉLYI M. (1976) Hydrodinamics of the Hungarian Basin. In Hydrogeology of Great Sedimentary Basins, Conference, IAHS Publication No. 120, pp. 146-163.
ERDÉLYI M. (1979) Hydrodynamics of the Hungarian Basin (VITUKI), Proc. No.18, Budapest.
FAURE G., CROCKET J. H. and HURLEY M. P. (1967) Some aspects of the geochemistry of strontium and calcium in the Hudson Bay and the Great lakes. Geochim. Cosmochim. Acta, Vol. 31, pp. 451-460.
FROELICH P.N., KLINKHAMMER G.P., BENDER M.L., LUEDTKE N.A., HEATH G.R., HAMMOND D., HARIMAN B. and MAYNARD V. (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta, Vol. 43, pp. 1075-1090.
HEIER K. S. and ADAMS J. A. S. (1964) The geochemistry of the alkali metals. Phys. Chem. Earth 5. pp. 255-380.
HELGESON H. C. (1971) Kinetics of mass transfer among silicates and aqueous solutions. Geochim. Cosmochim. Acta, Vol. 35, pp. 421-469.
HELGESON H. C., MURPHY W. M. and AAGAARD P. (1984) Thermodynamic and kinetic constraints on the reaction rates among minerals and aqeous solutions. II. Rate constants, effective surface area and the hydrolysis of feldspar. Geochim. Cosmochim. Acta Vol. 48, pp. 2405-2432.
HELLMANN R., EGGLESTON C. M., HOCHELLA M. F. JR. and CRERAR D. A. (1989) Altered layers on dissolving albite - 1. Results. In Water-Rock Interaction (ed. MILES D. L.), pp. 293-296. Balkema, Rotterdam.
HEM J. D. (1985) Study and Interpretation of the Chemical Characteristics of Natural Water. U. S. Geological Survey Water-Supply Paper 2254.
HOCHELLA M. F. JR. (1990) Atomic structure, microtopography, composition, and reactivity of mineral surfaces. Reviews in Mineralogy Vol. 23, Mineral-water interface geochemistry (eds HOCHELLA M. F. JR. and WHITE A. F.), Chap. 3, pp. 87-133.
LAXEN D. P. H. (1985) Trace metal adsorption /coprecipitation of hydrous ferric oxide under realistic conditions. Wat. Res. Vol. 19, pp. 1229 - 1236.
LION L. W., ALTMANN R. S. and LECKIE J. O. (1972) Trace - metal adsorption characteristics of estaurine particulate matter: evaluation of contribution of Fe/Mn oxide and organic surface coatings. Environ. Sci. Technol. Vol. 16, pp. 660-666.
LE MAITRE R. W. (1982) Numerical petrology. Developments in Petrology 8. Elsevier.
MURPHY W. M. and HELGESON H. C. (1987) Thermodynamic and kinetic constraints on the reaction rates among minerals and aqeous solutions. III. Activated complexes and the pH-dependence of the rates of feldspar, pyroxene, wollastonite, and olivine hydrolysis. Geochim. Cosmochim. Acta, Vol. 51, pp. 3137-3153.
NEWMAN M.C., ALBERTS J.J. and GREENHUT V.A. (1985) Geochemical factors complicating the use of Aufwuchs to monitor bioaccumulation of arsenic, cadmium, chromium, copper and zink. Water Res. Vol. 19, pp. 1157-1165.
OKUMURA M. and KITANO Y. (1985) Coprecipitation of alkali metal ions with calcium carbonate. Geochim. Cosmochim. Acta, Vol. 50, pp. 49 - 58.
PACES T. (1973) Steady-state kinetics and equilibrium between groundwater and granitic rock. Geochim. Cosmochim. Acta, Vol. 37, pp. 2641-2663.
PARKHURST D. L., THORSTENSON D. C. and PLUMMER L. N. (1990) PHREEQE - A computer program for geochemical calculation. U. S. Geol. Surv. Water-Resources Investigations, 80-96.
SAKATA M. (1985) Diagenetic remobilization of manganese, iron, copper and lead in anoxic sediment of a freshwater pond. Water Res. Vol. 19, pp. 1033-1038.
STUMM W. and MORGAN J. J. (1981) Aquatic Chemistry, 2nd Ed. John Wiley and Sons.
RÓNAI A. (1985) The Quaternary of the Great Hungarian Plain. Geol. Hung. Tom. 21, Inst. Geol. Hung. Budapest.
TAKAMATSU T., KAWASHIMA M. and KOYAMA M. (1985) The role of Mn^{2+} -rich hydrous manganese oxide in the accumulation of arsenic in lake sediments. Water Res. Vol. 19, pp. 1029-1032.
TESSIER A., CAMPBELL P. G. C. and BISSON M. (1980) Trace metal speciation in the Yamaska and St Francois rivers (Québec). Can. J. Earth. Sci. Vol.17, pp. 90 - 105.
VARSÁNYI, I. and Ó.KOVÁCS, L. (1994) Combination of statistical methods with modelling mineral-water interaction: a study of groundwater in the Great Hungarian Plain. Applied Geochemistry,Vol. 9, pp. 419-430.
VARSÁNYI, I. and Ó.KOVÁCS, L. (1997) Chemical evolution of groundwater in the River Danube deposits in the southern part of the Pannonian Basin (Hungary). Applied Geochemistry, Vol. 12, pp. 625-637.
WERSIN P., CHARLET L., KARTHEIN R. and STUMM W. (1989) From adsorption to precipitation: Sorption of Mn^{2+} on $FeCO_3$ (s) . Geochim. Cosmochim. Acta, Vol. 53, pp. 2787 - 2796.
WEDEPOHL K.H. (1968) Chemical Fractionation in the sedimentary enviroment. In: AHRENS L. H., (ed) Origin and distribution of the elements. Oxford: Pergamon Press.

WILSON, T.R.S., THOMPSON J., COLLEY S., HYDES D.J., HIGGS N.C. and SORENSEN J. (1985) Early organic diagenesis: The significance of progressive subsurface oxidation fronts in pelagic sediments. Geochim. Cosmochim. Acta, Vol. 49, pp. 811-821.

ZACHARA J. M., COWAN C. E. and RESCH C. T. (1991) Sorption of divalent metals on calcite. Geochim Cosmochim. Acta, Vol. 55, pp. 1549 - 1662.

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